PESTICIDE SURFACE WATER REPORT

MARCH 2003 SAMPLING EVENT



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Pesticide Monitoring Project Report March 2003 Sampling Event

Executive Summary

As part of the District's quarterly ambient monitoring program, unfiltered water samples from 39 sites were collected from March 10 to March 13, 2003, and analyzed for over sixty pesticides and/or products of their degradation. The herbicides 2,4-D, ametryn, atrazine, bromacil, diuron, hexazinone, norflurazon, prometon, and simazine, along with the insecticides/degradates atrazine desethyl, alpha endosulfan, beta endosulfan, and endosulfan sulfate were detected in one or more of these surface water samples.

The compounds and concentrations found are typical of those expected from intensive agricultural activity.

Background and Methods

The District's pesticide monitoring network includes stations designated in the Everglades National Park Memorandum of Agreement, the Miccosukee Tribe Memorandum of Agreement, the Lake Okeechobee Operating Permit, and the non-Everglades Construction Project (non-ECP) Permit. The District's canals and marshes depicted in Figure 1 are protected as Class III (fishable and swimable) waters, while Lake Okeechobee is protected as a Class I drinking water supply. Water Conservation Area 1 (WCA1) and the Everglades National Park are also designated as Outstanding Florida Waters, to which anti-degradation standards apply. Surface water and sediment are sampled quarterly and semiannually, respectively, upstream at each structure identified in the permit or agreement.

Sixty-four pesticides and degradation products were analyzed for in samples from all of the 39 sites (Figure 1). The analytes, their respective minimum detection limits (MDL), and practical quantitation limits (PQL) are listed in Table 1. All the analytical work is performed by the Florida Department of Environmental Protection (FDEP) Central Laboratory in Tallahassee Florida. The reader is referred to the *Quality Assurance Evaluation* section of this report for a summary of any limitations on data validity that might influence the utility of these data.

Each pesticide's description and possible uses and sites of application are taken from Hartley and Kidd (1987). The Florida Ground Water Guidance Concentrations (FGWGC) (FDEP, 1994) are listed to provide an indication at what level these pesticide residues could possibly impact human health, based on drinking water consumption or other routes of exposure (e.g., inhalation, ingestion of food residues, dermal uptake). Primary ground water standards are enforceable ground water standards, not screening tools or guidance levels. To evaluate the potential impacts on aquatic life, due to the pulsed nature of exposure, the maximum observed concentration is compared to the Criterion Maximum Concentration published by the USEPA under Section 304 (a) of the Clean Water Act, if available, or the lowest EC₅₀ or LC₅₀ reported in the summarized literature. This summary covers surface water samples collected from March 10 to

March 13, 2003.

Findings and Recommendations

At least one pesticide was detected in surface water at 38 of the 39 sites. The concentrations of the pesticides detected at each of the sites are summarized for the surface water in Table 2. All of these compounds have previously been detected in this monitoring program.

The above findings must be considered with the caveat that pesticide concentrations in surface water may vary significantly in relation to the timing and magnitude of pesticide application, rainfall events, pumping and other factors, and that this was only one sampling event. The possible long term or chronic toxicity impacts are also reported based on the single sampling event and do not take into account previous monitoring data.

Usage and Water Quality Impacts

<u>2,4-D</u>: 2,4-D is a selective systemic herbicide used for the post-emergence control of annual and perennial broad leaf weeds in terrestrial (grassland, established turf, sugarcane, rice, and on non-crop areas) as well as aquatic areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that 2,4-D (1) has minimum loss from soil by surface adsorption, with a moderate loss by leaching and surface solution; (2) is slightly toxic to mammals and relatively non-toxic to fish; and (3) does not bioaccumulate significantly. The 2,4-D concentrations detected should not have an acute impact on fish or aquatic invertebrates.

Ametryn: Ametryn is a selective terrestrial herbicide registered for use on sugarcane, bananas, pineapple, citrus, corn, and non-crop areas. Most algal effects occur at concentrations > $10 \,\mu\text{g/L}$ (Verschueren, 1983). Environmental fate and toxicity data in Tables 3 and 4 indicate that ametryn (1) is lost from soil relatively easily by leaching, surface adsorption, and in surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC₅₀ of 14.1 mg/L for goldfish (Hartley and Kidd, 1987). The ametryn surface water concentrations found in this sampling event ranged from 0.011 to 0.23 μ g/L. Using these criteria, these surface water concentrations should not have an acute, detrimental impact on fish or aquatic invertebrates.

Atrazine: Atrazine is a selective systemic herbicide registered for use on pineapple, sugarcane, corn, rangelands, ornamental turf and lawn grasses, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that atrazine (1) is easily lost from soil by leaching and in surface solution, with moderate loss from surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC₅₀ of 76 mg/L for carp, 16 mg/L for perch and 4.3 mg/L for guppies (Hartley and Kidd, 1987). Also, in a flow-through bioassay, the maximum acceptable toxicant concentration (MATC) of atrazine was 90 and 210 μ g/L for bluegill and fathead minnow (Verschueren,

1983). The Interim Reregistration Eligibility Decision for atrazine suggests that community-level and population-level effects in aquatic communities when exposed to concentrations of 10 to 20 μ g/L atrazine (U.S. EPA, 2003). The atrazine surface water concentrations found in this sampling event at 36 of the 39 sampling locations, ranged from 0.021 to 5.0 μ g/L. Using these criteria, these levels should not have an acute or chronic detrimental impact on fish or invertebrates.

Atrazine desethyl (DEA) and atrazine desisopropyl (DIA) are biotic degradation products of atrazine. These degradation products are both persistent and mobile in water; however, DEA is more stable and the dominant initial metabolite. Since DEA and DIA are structurally and toxicologically similar to atrazine, the concentrations of total atrazine residue (atrazine + DEA + DIA) may also be a significant consideration in the surface water environment. The DEA to atrazine ratio (DAR), on a molar basis, has been suggested as an indicator of nonpoint-source pollution of groundwater (Adams and Thurman, 1991) and as a tracer of ground water discharge into rivers (Thurman et al., 1992). Goolsby et al. (1997) determined that low DAR values, median <0.1, occur in streams during runoff shortly after application of atrazine. Higher DAR values, median about 0.4, occur later in the year after considerable degradation of atrazine to DEA has occurred in the soil. The low DAR ratio (0.1) at the locations where both atrazine and DEA were detected, suggests minimum degradation of atrazine (Table 5). However, these general guidelines were developed based on observations in Midwest watersheds in northern temperate climates with different soil and water management regimes as well as higher atrazine water concentrations. Applications to the south Florida environment should be made with caution.

Bromacil: Bromacil is a terrestrial herbicide registered for use on pineapple, citrus, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that bromacil (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96 hour LC_{50} of 164 mg/L for carp (Hartley and Kidd, 1987). The highest concentration of bromacil detected in the surface water during this sampling event was at CR33.5T (0.077 μ g/L). Using these criteria, these levels should not have an acute or chronic detrimental impact on fish.

<u>Diuron</u>: Diuron is a selective, systemic terrestrial herbicide registered for use on sugarcane, bananas, and citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that diuron (1) is easily lost from soil in surface solution, with moderate loss from leaching or surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data includes a 96-hour LC_{50} of 25 mg/L for guppies (Hartley and Kidd, 1987). Crustaceans are affected at lower concentrations with a 48 hour LC_{50} of 1.4 mg/L for water fleas and a 96 hour LC_{50} of 0.7 mg/L for water shrimp (Verschueren, 1983). Most algal effects occur at concentrations > 10 μ g/L (Verschueren, 1983). The only surface water concentration of diuron found

during this sampling event was $0.32 \mu g/L$ (Table 2). Using these criteria, this level should not have an acute, harmful impact on fish or algae.

Endosulfan: Endosulfan is a non-systemic insecticide and acaricide registered for use on many crops, including beans, tomatoes, corn, cabbage, citrus, and ornamental plants. Technical endosulfan is a mixture of the two stereoisomeric forms, the α (alpha) and the β (beta) forms. Endosulfan is highly toxic to mammals, with an acute oral LD₅₀ for rats of 70 mg/Kg (Hartley and Kidd, 1987). The Soil Conservation Service rates endosulfan with an extra small potential for loss due to leaching, a large potential for loss due to surface adsorption and a moderate potential for loss in surface solution (Table 3). β -endosulfan's water solubility and Henry's constant indicate volatilization may be significant in shallow waters. A bioconcentration factor of 1,267 indicates a low to moderate degree of accumulation in aquatic organisms (Lyman et al., 1990). Endosulfan (α and/or β) was detected at two locations (S177 and S178) in the south Miami-Dade farming area (Table 2). However, these concentrations do not exceed the Florida Class III surface water quality standard (Chapter 62-302) (Figure 2).

Endosulfan sulfate: Endosulfan sulfate is an oxidation metabolite of the insecticide endosulfan. The water solubility and Henry's constant indicate that endosulfan sulfate is less volatile than water and concentrations will increase as water evaporates (Lyman et al., 1990). Endosulfan sulfate has a relatively high degree of accumulation in aquatic organisms (Table 4). The surface water detection occurred at S178 (0.14 μg/L). No FDEP surface water standard (FAC 62-302) has been promulgated for endosulfan sulfate.

Hexazinone: Hexazinone is a non-selective contact herbicide that inhibits photosynthesis. Registered uses include sugarcane, pineapple, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that hexazinone (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Hexazinone is practically non-toxic to freshwater invertebrates with an EC₅₀ of 145 mg/l for *Daphnia magna* (U.S. Environmental Protection Agency, 1988). The highest surface water concentration detected in this sampling event at FECSR78 (0.031 μg/L) should not have an acute impact on fish or aquatic invertebrates.

Norflurazon: Norflurazon is a selective herbicide registered for use on many crops including citrus. Environmental fate and toxicity data in Tables 3 and 4 indicate that norflurazon (1) is easily lost from soil surface solution and a moderate potential for loss due to leaching and surface adsorption; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The LC₅₀ for norflurazon is >200 mg/L for catfish and goldfish (Hartley and Kidd, 1987). The norflurazon surface water concentrations ranged from 0.020 to 0.64 μ g/L. Even at the highest concentration, this is several orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates.

<u>Prometon</u>: Prometon is a non-selective systemic herbicide registered for use in non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that prometon (1) is easily lost from soil by leaching, with moderate loss from surface adsorption or surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. The only concentration of prometon detected (0.036 μ g/L at NSIDWC07) is several orders of magnitude below the calculated chronic action level. Using these criteria, these levels should not have an acute, detrimental impact on fish or aquatic invertebrates.

Simazine: Simazine is a selective systemic herbicide registered for use on many crops including sugarcane, citrus, corn, and non-crop areas. Environmental fate and toxicity data in Tables 3 and 4 indicate that simazine (1) is easily lost from soil by leaching and has a moderate potential for loss due to surface adsorption and surface solution; (2) is relatively non-toxic to mammals and fish; and (3) does not bioconcentrate significantly. Additional fish toxicity data include a 96 hour LC50 of 49 mg/L for guppies (Hartley and Kidd, 1987). Most of the aquatic biological effects occur at concentrations > 500 μ g/L (Verschueren, 1983). Aquatic invertebrate LC50 toxicity ranges from 3.2 mg/L to 100 mg/L for simazine (U.S. Environmental Protection Agency, 1984). The highest surface water concentration of simazine was detected at S6 (0.048 μ g/L), below any level of concern for fish or aquatic invertebrates.

Quality Assurance Evaluation

Replicate samples were collected at sites S140 and S4. All the analytes detected in the surface water had precision \leq 30% RPD. No analytes were detected in the field blanks collected at S4, S18C, S38B, and S31. All samples were shipped and all bottles were received.

Low concentrations of representative analytes from each pesticide group/method were added to laboratory water as well as to samples submitted. The matrix spike recoveries for chlorpyrifos methyl did not meet the specified requirements for the surface water samples collected at the following locations: S79, CR33.5T, S78, S235, FECSR78, S65E, S191, S18C (including field blank), S178, S177, S332, S176, S331, S355A, S355B, S12C, and US41-25. In addition to the chlorpyrifos methyl, atrazine desethyl matrix spike recoveries did not meet the specified requirements for surface water at: S31 (including field blank), S9, S142, G123, S140 (including replicate), S190, L3BRS, S8, S7, NSIDWC06, NSIDWC07, S38B (including field blank), S6, S5A, ACME1DS, G94D, C25S99, GORDYRD, S80, S2, S3, and S4 (including replicate). The remainder of the analytes for each sample adhered to the targets for precision and accuracy as outlined in the FDEP Comprehensive Quality Assurance Plan. Organic quality assurance targets are set according to historically generated data or are adapted from the U.S. Environmental Protection Agency with slight modifications or internal goals, based on FDEP limited data. Parameters with low or high recoveries indicate that the sample matrix interferes with these analyses and interpretation of the respective analytical results should consider this effect.

Glossary

- LD₅₀: The dosage which is lethal to 50% of the terrestrial animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- LC₅₀: A concentration which is lethal to 50% of the aquatic animals tested within a short (acute) exposure period, usually 24 to 96 hours.
- EC₅₀: A concentration necessary for 50% of the aquatic species tested to exhibit a toxic effect short of mortality (e.g., swimming on side or upside down, cessation of swimming) within a short (acute) exposure period, usually 24 to 96 hours.
- Koc: The soil/sediment partition or sorption coefficient normalized to the fraction of organic carbon in the soil. This value provides an indication of the chemical's tendency to partition between soil organic carbon and water.

Bioconcentration Factor:

The ratio of the concentration of a contaminant in an aquatic organism to the concentration in water, after a specified period of exposure via water only. The duration of exposure should be sufficient to achieve a near steady-state condition.

Soil or water half-life:

The time required for one-half the concentration of the compound to be lost from the water or soil under the conditions of the test.

- MDL: The minimum concentration of an analyte that can be detected with 99% confidence of its presence in the sample matrix.
- PQL: The lowest level of quantitation that can be reliably achieved within specified limit of precision and accuracy during routine laboratory operating conditions. The PQL is further verified by analyzing spike concentrations whose relative standard deviation in 20 fortified water samples is < 15%. In general, the PQL is 2 to 5 times larger than the MDL.

References

Adams, C.D. and E.M. Thurman. (1991). Formation and Transport of Deethylatrazine in the Soil and Vadose Zone. J. Environ. Qual. Vol. 20 pp. 540-547.

Federal Register: March 22, 2002; Volume 67, Number 56, pages 13327 – 13328; Ethion Cancellation Order.

Florida Department of Environmental Protection (1994). Florida Ground Water Guidance Concentrations. Tallahassee, FL.

Goolsy, D.A., E.M. Thurman, M.L. Pomes, M.T. Meyer, and W.A. Battaglin. (1997).

Herbicides and Their Metabolites in Rainfall: Origin, Transport, and Deposition Patterns across the Midwestern and Northeastern United States, 1990-1991. Environ. Sci. Technol. Vol. 31, No. 5, pp. 1325-1333.

Goss, D. and R. Wauchope. (Eds.) (1992). *The SCS/ARS/CES Pesticide Properties Database: II Using It With Soils Data In A Screening Procedure*. Soil Conservation Service. Fort Worth, TX.

Hartley, D. and H. Kidd. (Eds.) (1987). *The Agrochemicals Handbook*. Second Edition, The Royal Society of Chemistry. Nottingham, England.

Johnson, W.W. and M.T. Finley. (1980). *Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates*. U.S. Department of the Interior, Fish and Wildlife Service Resource Publication 137. Washington, DC.

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. (1990). *Handbook of Chemical Property Estimation Methods*. American Chemical Society, Washington, DC.

Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsa, MI.

Schneider, B.A. (Ed.) (1979). *Toxicology Handbook, Mammalian and Aquatic Data, Book 1: Toxicology Data*. U.S. Environmental Protection Agency. U.S. Government Printing Office. Washington, DC. EPA-5400/9-79-003

Thurman, E.M., Goolsby, D.A., Meyer, M.T., Mills, M.S., Pomes, M.L., and Kolpin, D.W. (1992). A Reconnaissance Study of Herbicides and Their Metabolites in Surface Water of the Midwestern United States Using Immunoassay and Gas Chromatography/Mass Spectrometry. Environ. Sci. Technol., Vol. 26, No. 12. pp. 2440-2447.

U.S. Environmental Protection Agency (1972).). Effects of Pesticides in Water: A Report

to the States. U.S. Government Printing Office. Washington, D.C.
(1984). Chemical Fact Sheet for Simazine. March, 1984.
(1988). Chemical Fact Sheet for Hexazinone. September, 1988.
(1991) Pesticide Ecological Effects Database, Ecological Effects Branch, Office of Pesticide Programs, Washington, DC.
(1996). <i>Drinking Water Regulations and Health Advisories</i> . Office of Water. EPA 822-B-96-002.
(2003). Interim Reregistration Eligibility Decision for Atrazine, Case No. 0062. Office of Prevention, Pesticides, and Toxic Substances. Washington, D.C.

Verschueren, K. (1983). *Handbook of Environmental Data on Organic Chemicals*. Second Edition, Van Nostrand Reinhold Co. Inc. New York, NY.

Figure 1. South Florida Water Management District Pesticide Monitoring Network.

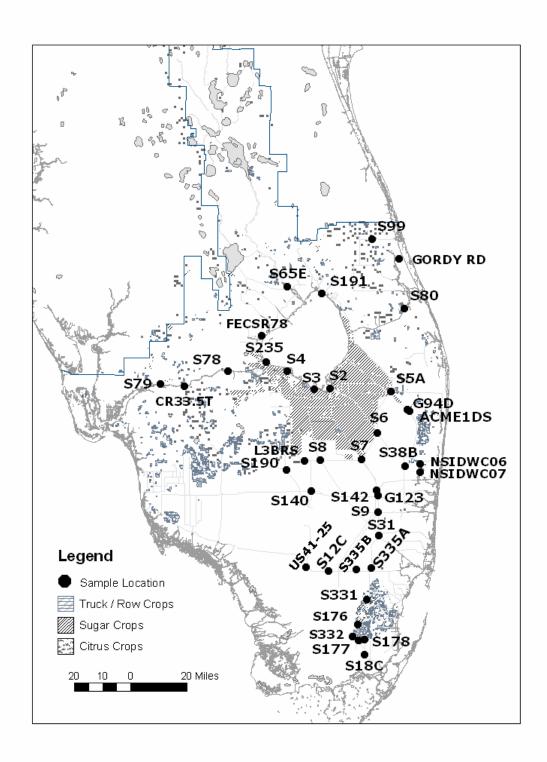


Table 1. Minimum detection limits (MDL) and practical quantitation limits (PQL)

for pesticides detected in March 2003.

for pesticides detected in	<u> </u>		
Pesticide or metabolite	Water Range of MDL-PQL (μg/L)	Pesticide or metabolite	Water Range of MDL-PQL (μg/L)
2,4-D	0.2 - 0.6	β-endosulfan (beta)	0.0038 - 0.0176
2,4,5-T	0.2 - 3	endosulfan sulfate	0.0045 - 0.0212
2,4,5-TP (silvex)	0.2 - 3	endrin	0.019 - 0.76
alachlor	0.047 - 1.92	endrin aldehyde	0.0042 - 0.0196
aldrin	0.0019 - 0.038	ethion	0.019 - 0.088
ametryn	0.0094 - 0.044	ethoprop	0.019 - 0.088
atrazine	0.0094 - 0.384	fenamiphos (nemacur)	0.028 - 0.132
atrazine desethyl	0.0094 - 0.044	fonofos (dyfonate)	0.019 - 0.088
atrazine desisopropyl	0.0094 - 0.044	heptachlor	0.0023 - 0.092
azinphos methyl (guthion)	0.019 - 0.088	heptachlor epoxide	0.0019 - 0.076
α-BHC (alpha)	0.0021 - 0.0096	hexazinone	0.019 - 0.088
β-BHC (beta)	0.0019 - 0.0132	imidacloprid	0.2 - 0.6
δ-BHC (delta)	0.0019 - 0.0096	linuron	0.2 - 0.6
γ-BHC (gamma) (lindane)	0.0019 - 0.192	malathion	0.028 - 0.132
bromacil	0.038 - 0.176	metalaxyl	0.047 - 0.224
butylate	0.019 - 0.088	methoxychlor	0.0098 - 1
carbophenothion (trithion)	0.015 - 0.072	metolachlor	0.057 - 2.28
chlordane	0.0094 - 0.076	metribuzin	0.019 - 0.76
chlorothalonil	0.015 - 0.072	mevinphos	0.057 - 0.356
chlorpyrifos ethyl	0.019 - 0.088	mirex	0.011 - 0.052
chlorpyrifos methyl	0.0094 - 0.044	naled	0.075 - 0.356
cypermethrin	0.019 - 0.088	norflurazon	0.019 - 0.088
DDD-P,P'	0.0045 - 0.0212	parathion ethyl	0.019 - 0.088
DDE-P,P'	0.0038 - 0.0176	parathion methyl	0.019 - 0.088
DDT-P,P'	0.0038 - 0.0176	PCB	0.019 - 0.088
demeton	0.11 - 0.52	permethrin	0.015 - 0.072
diazinon	0.019 - 0.088	phorate	0.028 - 0.132
dicofol (kelthane)	0.042 - 0.196	prometryn	0.019 - 0.088
dieldrin	0.0019 - 0.076	prometon	0.019 - 0.088
disulfoton	0.019 - 0.088	simazine	0.0094 - 0.38
diuron	0.2 - 0.6	toxaphene	0.071 - 0.388
α-endosulfan (alpha)	0.0038 - 0.0176	trifluralin	0.0075 - 0.76

Table 2. Summary of pesticide residues (µg/L) above the method detection limit found in surface water samples collected by SFWMD in March 2003.

Date Site Site	Table 2. 3	Summary o	тре	esticiae	residues	s (µg/L) a	bove the	metnoa a	etection	i iimit ioun	d in Suriac	e water sa	imples colle	ected by S		March 20	
STICE N - 0.052 - - - - - - - - -	Date	Site	-low	2,4-D	ametryn	atrazine		bromacil	diuron				hexazinone	norflurazon	prometon	simazine	Number of compounds detected at site
S176 Y - 0.052 - - - - - - - - 1	3/10/2003	S12C		-	-	0.052	-	_	-	-	-	-	-	_	-	-	1
S177 Y - 0.022 1 - 0.0000 0.0012 - 0.0002 3	0.10.2000			_	-		_	_	-	-	_	_	_	_	_	_	1
S18C N				-	-		-	-	-	0.0080 I	-	0.012 I	-	-	-	-	3
S331 N - 0.095 - - - - - - - - 0.05		S178	Ν	-	-	0.022 I	-	-	-	0.018	0.0097 I	0.14	-	-	-	-	4
S331 N		S18C	Ν	-	-	0.038 I	-	-	-	-	-	0.012 I	-	-	-	-	2
S332 N		S331	Ν	-	-		-	-	-	-	-		-	-	-	-	1
S355B N - - 0.021 0.012 - - - - - - - - 2			Ν	-	-	-	-	-	-	-	-	-	-	-	-	-	0
US41-25 N		S355A	Ν	-	-	0.024 I	-	-	-	-	-	-	-	-	-	-	1
3/11/2003		S355B	Ν	-	-	0.21	0.012 I	-	-	-	-	-	-	-	-	-	2
L3BRS N - - 0.10 - - - - - - - - -		US41-25	Ν	-	-	0.021 I	-	-	-	-	-	-	-	-	-	-	1
S140	3/11/2003	G123	R	-	0.021 I	0.22	0.012 I	-	-	-	-	-	-	-	-	-	3
S142 Y - 0.013 0.15 0.0097 3		L3BRS	Ν	-	-	0.10	_	_	-	-	-	-	-	_	-	-	1
S190 N - - 0.030 - - - - - - - - -		S140	Ν	-	-	0.11 *	-	0.041 I*	-	-	-	-	-	0.084 *	-	-	3
S31 N - - 0.031 - - - - - - - - -		S142	Υ	-	0.013 I	0.15	0.0097 I	-	-	-	-	-	-	-	-	-	3
S7 N - 0.075		S190	Ν	-	-	0.030 I	-	-	-	-	-	-	-	0.037 I	-	-	2
S8 N -		S31	Ν	-	-	0.031 I	-	-	-	-	-	-	-	-	-	-	1
S9		S7	Ν	-	0.075	1.3	-	-	-	-	-	-	-	-	-	-	2
3/12/2003 ACME1DS N - 0.030 0.24 0.014 - - - - - - - - -			Ν	-	0.23	4.6	-	-	-	-	-	-	-	-	-	0.018 I	3
C25S99 N - - - - - - - - -		S9	Ν	-	-	0.035 I	-	-	-	-	-	-	-	-	-	-	1
G94D N -	3/12/2003	ACME1DS	Ν	-	0.030 I	0.24	0.014 I	-	-	-	-	-	-	-	-	-	3
GORDYRD Y -		C25S99	Ν	-	-	-	-	-	-	-	-	-	0.023 I	0.64	-	0.045	
NSIDWC06 N -			Z	-	0.027 I	0.15	0.010 I	-	-	-	-	-	-	-	-	-	3
NSIDWC07 N -				-	-	-	-	-	-	-	-	-	-	0.36	-	0.018 I	2
S2			Z	-	0.011 I		-	1	0.32 I	-	1	-	-	-	-	-	3
S3 N - 0.011 0.35 0.031 - - - - - - - - -				-	0.021 I		-	1	-	-	-	-	-	1	0.036 I		4
S38B N 2.3 0.012 1 1.4 - - - - - - - - -				-	-	0.28	0.032 I	1	-	-	-	-	-	-	-	0.012 I	3
S4			Z	-	0.011 I	0.35	0.031 I	1	-	-	1	-	-	-	-	0.010 I	
S5A N -				2.3		1.4	-	1	-	-	1	-	-	-	-	-	3
S6 N - 0.21 5.0 - - - - - - - - 0.048 3 3/13/2003 CR33.5T N - - 0.15 0.017 I 0.077 I - - - - 0.17 - 0.039 5 FECSR78 Y - - 0.086 - - - - - 0.031 I - - - 2 S191 N 0.48 I - 0.05 - - - - - 0.031 I - - - - 2 S191 N 0.48 I - 0.05 - - - - - 0.030 I -				-				-	-	-	-	-	-	-	-	-	3
S80 - - 0.92 - - - - - - 0.20 - 0.026 3				-	0.016 I	0.47	0.037 I	-	-	-	-	-	-	-	-		4
3/13/2003 CR33.5T N - - 0.15 0.017 0.077 - - - - - - 0.031 - - - 2			Ν	-	0.21		-	-	-	-	-	-	-	-	-		3
FECSR78 Y 0.086 0.031 I 2 S191 N 0.48 I - 0.05 0.030 I 3 S235 N - 0.20 0.020 I 0.047 I - 0.011 I 4 S65E Y - 0.092 0.012 I 0.020 I 3 S78 Y - 0.20 0.022 I 0.020 I 3 S79 Y 0.15 0.018 I 0.052 I 0.14 - 0.024 I 5			1	-	-			1	-	-	-	-	-		-		
S191 N 0.48 I - 0.05 - - - - - 0.030 I - - - 3 S235 N - - 0.020 0.020 I - - - - - 0.047 I - 0.011 I 4 S65E Y - - 0.092 0.012 I - - - - - - 0.020 I 3 S78 Y - - 0.02 0.022 I - - - - - 0.020 I - - 3 Total number of compound - - - - - - - 0.024 I 5	3/13/2003		Ν	-	-	0.15	0.017 I	0.077 I	-	-	-	-	-	0.17	-	0.039	
S235 N - - 0.020 1 - - - - - 0.047 1 - 0.011 1 4 S65E Y - - 0.092 0.012 1 - - - - - - - 0.020 1 3 S78 Y - - 0.02 1 - - - - - 0.020 1 - - 3 S79 Y - - 0.15 0.018 1 0.052 1 - - - - 0.14 - 0.024 1 5		FECSR78		-	-	0.086	-	ı	-	-	-	-	0.031 I	-	-	-	2
S65E Y - - 0.092 0.012 I - - - - - - - 0.020 I 3 S78 Y - - 0.022 I - - - - - 0.020 I - - 3 S79 Y - - 0.15 0.018 I 0.052 I - - - - 0.14 - 0.024 I 5				0.48 I	-			-	-	-	-	-	0.030 I	-	-	-	
S78 Y - - 0.020 0.022 I - - - - - 0.020 I - - 3 S79 Y - - 0.15 0.018 I 0.052 I - - - - 0.14 - 0.024 I 5			N	-	-			-	-	-	-	-	-	0.047 I	-		
S79 Y 0.15 0.018 0.052 0.14 - 0.024 5			Υ	-	-			-	-	-	-	-	-	-	-	0.020 I	
Total number of compound			Υ	-	-	0.20		-	-	-	-	-	-	0.020 I	-	-	
Total number of compound 2 13 36 14 3 1 2 1 3 3 0 4 12		S79	Υ	-	- 1	0.15	0.018 I	0.052 I	-	-	-	-	-	0.14	_	0.024 I	5
detections 2 13 30 14 3 1 2 1 3 3 9 1 13				2	13	36	14	3	1	2	1	3	3	9	1	13	

N - no Y - yes R - reverse; - denotes that the result is below the MDL; * results are the average of duplicate samples I - value reported is less than the minimum quantitation limit, and greater than or equal to the minimum detection limit

Table 3. Selected properties of pesticides found in March 2003 sampling event.

	Surface	Ground	LD50								
	Water	Water	acute rats		Water		soil				
	Standards	Guidance	oral	EPA	Solubility	Koc	half-life				
	FAC 62-302	Conc.	(mg/kg)	carcinogenic	(mg/L)	(mL/g)	(days)	SCS	S rating	g (2)	Bioconcentration
common name	(µg/L)	(µg/L)	(1)	potential	(2, 3)	(2, 3)	(2, 3)	LE	SA	SS	Factor (BCF)
2,4-D (acid)	(100)	70**	375	D	890	20	10	М	S	М	13
ametryn	-	63	1110	D	185	300	60	М	М	М	33
atrazine	-	3**	3080	С	33	100	60	L	М	L	86
bromacil	-	90	5200	С	700	32	60	L	M	М	15
diuron	-	14	3400	D	42	480	90	М	M	L	75
endosulfan-alpha	0.056	0.35	70	-	0.53	12400	50	XS	L	М	884
endosulfan-beta	-	0.35	70	-	0.28	-	-	-	-	-	1267
endosulfan-sulfate	-	0.3	-	-	0.117	-	-	-	-	-	2073
hexazinone	-	231	1690	D	33000	54	90	L	М	М	2
norflurazon	-	280	9400	С	28	700	90	М	М	Ĺ	94
prometon	-	105	2980	-	720	200	500	L	М	М	15
simazine	-	4**	>5000	С	6.2	130	60	L	М	М	221

SCS Ratings are pesticide loss due to leaching (LE), surface adsorption (SA) or surface solution (SS) and grouped as large(L), medium (M), small (S) or extra small (XS) Bioconcentration Factor (BCF) calculated as BCF = $10^{(2.791 - 0.564 \log WS)}$ (4)

B2: probable human carcinogen; C: possible human carcinogen; D: not classified; E: evidence of non-carcinogen for humans (5)

FDEP surface water standards (4/95) for Class III waters except Class I in ()

Note: endosulfan usually considered the sum of alpha and beta isomers

- (1) Hartley, D. and H. Kidd. (Eds.) (1987). The Agrochemicals Handbook. Second Edition, The Royal Society of Chemistry. Nottingham, England.
- (2) Goss, D. and R. Wauchope. (Eds.) (1992). The SCS/ARS/CES Pesticide Properties Database: II Using It With Soils Data In A Screening Procedure. Soil Conservation Service. Fort Worth, TX.
- (3) Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsa, MI.
- (4) Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. (1990). Handbook of Chemical Property Estimation Methods. American Chemical Society, Washington, DC.
- (5) U.S. Environmental Protection Agency (1996). Drinking Water Regulations and Health Advisories. Office of Water. EPA 822-B-96-002.

^{**} primary standard

Table 4. Toxicity of pesticides found in the March 2003 sampling event to freshwater aquatic invertebrates and fishes (ug/L).

						•	• • = ١		9	• • •			. 9 0.0.1.0			· · · · · · · · · · · · · · · · · · ·	onco (agri	-/:						
	48 hr EC	50			96 hr LC	50			96 hr LC5	0			96 hr L0	C50			96 hr LC5	0			96 hr LC	50		
	Water fl	ea			Fathead Minnow (Bluegill				Largemo Bass				Rainbow Tr (#)	out			Channe Catfish			
common	Daphni	a	acute	chronic	Pimephal	es	acute	chronic	Lepomis		acute	chronic	Micropte	erus	acute	chronic	Oncorhynci	hus	acute	chronic	Ictalurus	S	acute	chronic
name	magna	9	toxicity (*)	toxicity (*)	promela	s	toxicity	toxicity	macrochiru	ıs	toxicity	toxicity	salmoid	les	toxicity	toxicity	mykiss		toxicity	toxicity	punctatu	s	toxicity	toxicity
2,4-D	25,000	(7)	8333	1250	133,000	(7)	44333	6650	180,000	(8)	60000	9000	-		-	-	100,000	(4)	33333	5000	•		-	-
	-		-	-	-		-	-	900 (48 hr)	(6)	-	-	-		-	-	110,000	(7)	36667	5500	•		-	-
ametryn	28,000	(7)	9333	1400	-		-	-	4,100	(4)	1367	205	-		-	-	8,800	(4)	2933	440			-	-
atrazine	6900	(7)	2300	345	15,000	(7)	5000	750	16,000	(4)	5333	800	-		-	-	8,800	(4)	2933	440	7,600	(4)	2533	380
bromacil	-		-	-	-		-	-	127,000	(7)	42333	6350	-		-	-	36,000	(7)	12000	1800			-	-
diuron	1,400	(7)	467	70	14,200	(7)	4733	710	5,900	(4)	1967	295	-		-	-	5,600	(4)	1867	280	ı		-	-
endosulfan	166	(7)	55	8	1	(1)	0.3	0.05	1	(1)	0.33	0.05	-		-	-	1	(1)	0.33	0.050	1	(1)	0.3	0.05
	-		-	-	-		-	-	2	(3)	0.67	0.10	-		-	-	3	(2)	1	0.15	1.5	(7)	0.5	0.08
	-		-	-	-		-	-	-		-	-	-		-	-	1	(3)	0.33	0.050	1		-	-
	-		-	-	-		-	-	-		-	-	-		-	-	0.3	(5)	0.10	0.015	•		-	-
hexazinone	151,600	(7)	50533	7580	274,000	(4)	91333	13700	100,000	(7)	33333	5000	-		-	-	180,000	(7)	60000	9000	•		-	-
norflurazon	15,000	(7)	5000	750	-		-	-	16,300	(7)	5433	815	-		-	-	8,100	(7)	2700	405	>200,000	(4)	>67,000	>10,000
prometon	-		-	-	-		-	-	40,000	(5)	13333	2000	-		-	-	12,000	(5)	4000	600			-	-
simazine	1,100	(7)	367	55	100,000	(7)	33333	5000	90,000	(4)	30000	4500	-		-	-	100,000	(7)	33333	5000	-		-	-

^(*) Florida Administrative Code (FAC) 62-302.200, for compounds not specifically listed, acute and chronic toxicity standards are calculated as one-third and one-twentieth, respectively, of the amount lethal to 50% of the test organisms in 96 hours, where the 96 hour LC50 is the lowest value which has been determined for a species significant to the indigenous aguatic community.

- (#) Species is not indigenous. Information is given for comparison purposes only.
- (1) Johnson, W. W. and M.T. Finley (1980). Handbook of Acute Toxicity of Chemicals to Fish and Aquatic Invertebrates. U.S. Department of the Interior, Fish and Wildlife Service Resource Publication 137. Washington, DC.
- (2) U.S. Environmental Protection Agency (1977). Silvacultural Chemicals and Protection of Water Quality. Seattle, WA. EPA-910/9-77-036.
- (3) Schneider, B.A. (Ed.) (1979). Toxicology Handbook, Mammalian and Aquatic Data, Book 1: Toxicology Data. U.S. Environmental Protection Agency. U.S. Government Printing Office. Washington, DC. EPA-5400/9-79-003
- (4) Hartley, D. and H. Kidd. (Eds.) (1987). The Agrochemicals Handbook. Second Edition, The Royal Society of Chemistry. Nottingham, England.
- (5) Montgomery, J.H. (1993). Agrochemicals Desk Reference: Environmental Data. Lewis Publishers. Chelsa, Ml.
- (6) Verschueren, K. (1983). Handbook of Environmental Data on Organic Chemicals. Second Edition, Van Nostrand Reinhold Co. Inc. New York, NY.
- (7) U.S. Environmental Protection Agency (1991) Pesticide Ecological Effects Database, Ecological Effects Branch, Office of Pesticide Programs, Washington, DC.
- (8) Mayer, F.L., and M.R. Ellersieck. (1986). Manual of Acute Toxicity: Interpretation and Database for 410 Chemicals and 66 Species of Freshwater Animals. United States Fish and Wildlife Service Publication No. 160.

Table 5. Atrazine Desethyl/Atrazine ratio (DAR) data March 2003.

Date	Site	Flow	atrazine ug/l	moles/l	atrazine desethyl ug/l	moles/l	DAR
3/10/2003	S355B	N	0.21	9.73642E-10	0.012	6.39551E-11	0.1
3/11/2003	G123	R	0.22	1.02001E-09	0.012	6.39551E-11	0.1
	S142	Υ	0.15	6.95458E-10	0.0097	5.16971E-11	0.1
3/12/2003	ACME1DS	N	0.24	1.11273E-09	0.014	7.46143E-11	0.1
	G94D	N	0.15	6.95458E-10	0.01	5.3296E-11	0.1
	S2	N	0.28	1.29819E-09	0.032	1.70547E-10	0.1
	S3	N	0.35	1.62274E-09	0.031	1.65217E-10	0.1
	S4	N	0.4367	2.02471E-09	0.022	1.17251E-10	0.1
	S5A	N	0.47	2.17910E-09	0.037	1.97195E-10	0.1
3/13/2003	CR33.5T	N	0.15	6.95458E-10	0.017	9.06031E-11	0.1
	S235	N	0.2	9.27278E-10	0.02	1.06592E-10	0.1
	S65E	Υ	0.092	4.26548E-10	0.012	6.39551E-11	0.1
	S78	Υ	0.2	9.27278E-10	0.022	1.17251E-10	0.1
	S79	Υ	0.15	6.95458E-10	0.018	9.59327E-11	0.1
				DAR	All sites	Flow only sites	No flow sites
				average	0.1	0.1	0.1
				median	0.1	0.1	0.1
				minimum	0.1	0.1	0.1
				maximum	0.1	0.1	0.1

Figure 2. Endosulfan Concentration in Surface Water at S178

